

# PATENT ABSTRACTS OF JAPAN

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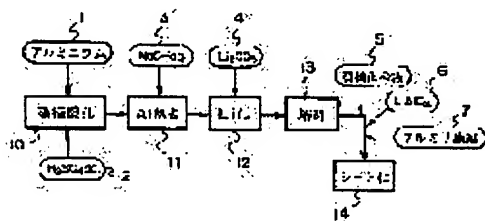
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## (54) MANUFACTURE OF ELECTROLYTE PLATE FOR FUSED CARBONATE FUEL CELL AND ELECTROLYTE PLATE FOR FUSED CARBONATE FUEL CELL



(57)Abstract:

PROBLEM TO BE SOLVED: To reduce a loss quantity of electrolyte, and maintain battery initial performance over a long period of time by using an anodic oxidation type lithium aluminate particle and alimina fiber as a reinforcing material in an electrolyte plate.

SOLUTION: An aluminium oxide having a porous structure is manufactured by electrochemically oxidizing metallic Al 1 in

a sulfuric acid aqueous solution 2. Al remaining without being anodically oxidized is selectively dissolved by using a basic aqueous solution 3 such as NaOH. The aluminium oxide formed by anodic oxidation is turned into lithium by using lithium salt 4 such as  $\text{Li}_2\text{CO}_3$ , and is formed as anodic oxidation type lithium aluminate, and this is cracked into a submicron particle. Next, an electrolyte plate sheet is manufactured by using an organic compound 5 as a binding agent and a plasticizer, an anodic oxidation type lithium particle obtained in a process so far and a lithium aluminate particle 6 except it and an additive 7 of either one of base board strength improving alumina fiber and lithium aluminate fiber.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a fuel cell, especially relates to the manufacture approach, the electrolyte plate for fused carbonate fuel cells, and fused carbonate fuel cell of the electrolyte plate for fused carbonate fuel cells.

[0002]

[Description of the Prior Art] The fused carbonate fuel cell forms the cell single cel by using the separator for dividing the cell which adjoins at the time of a collecting electrode plate, the passage formation wavelike plate of fuel gas and oxidant gas, and a laminating on the basis of the structure which arranged the cathode which uses as a principal component the anode which uses nickel as a principal component up and down and nickel oxide of the ulmin acid lithium porous body which is made to carry out impregnation of the melting alkali-metal carbonate, and uses it.

[0003] An electrolyte plate prevents the cross of fuel gas and oxidant gas, or leak out of a cell while insulating a positive electrode and a negative electrode electrically, and it has the role which holds the fused electrolyte of an ion conductor in a substrate further. In order to fulfill such conditions, the porosity substrate which consisted of submicron ulmin acid lithium particles is used. Moreover, in order not to check the ionic conduction of a melting carbonate, it is supposed that it is required to use an electrolyte plate as much as possible with big porosity.

[0004] The improvement proposal which raises electrolyte retention volume is made changing ceramic particle size and decreasing electrolyte dissipation to the polar zone to such a problem, with the electrolyte plate which touches the electrode of the inside which carries out two or more sheet laminating, and other electrolyte plates. There is JP,63-284764,A as the example.

Moreover, the mean particle diameter within a field is changed and it is proposed by JP,4-286868,A about the electrolyte plate which gas-seal nature was raised and heightened electrolyte maintenance capacity.

[0005]

[Problem(s) to be Solved by the Invention] However, there is a possibility that a fused electrolyte may localize that the pore distribution in an electrolyte plate is uneven. Moreover, at a part with a large pole diameter, since relative capillary force becomes weaker, electrolyte abundance runs short, and there is also a possibility that ionic conduction resistance may increase. Furthermore, partial creep deformation of an electrolyte plate had also become a problem.

[0006] The electrolyte held at the electrolyte plate of a fused carbonate fuel cell is the generation reaction of creepage, evaporation, or a high resistance corrosion layer etc., and decrease in number with operation-time progress. The reduction in electrolytic causes the increment in ionic conduction resistance, and causes cell performance degradation. For this reason, electrolyte

holding power is high and an electrolyte plate with the uniform pore distribution within a field in which big and rough pore 1 micrometers or more does not exist is required.

[0007] In order to solve such a technical problem, this invention can hold many electrolytes, and when the resistance to ionic conduction forms pore [ that it is uniform and minor diameter ] small, it uses the manufacture approach, the electrolyte plate for fused carbonate fuel cells, and fused carbonate fuel cell of the high electrolyte plate for fused carbonate fuel cells of electrolyte holding power as an offer plug.

[0008]

[Means for Solving the Problem] The manufacture approach of the electrolyte plate for fused carbonate fuel cells built over this invention in order to solve such a technical problem The anodic oxidation aluminum which carries out anodic oxidation of the metal aluminum substrate electrochemically in aqueous acids, and has pore is formed. Carry out selective dissolution of the aluminum of the substrate ingredient which remained without oxidizing, remove, and it leaves porous anodic oxidation aluminum. Lithiate this anodization aluminum and it considers as the ulmin acid lithium of an anodization mold. This anodization type of ulmin acid lithium is cracked to a submicron particle, the ulmin acid lithium particle of an anodization mold is formed, and it is characterized by creating an electrolyte plate, using this anodization type of ulmin acid lithium particle as an electrolyte maintenance ingredient.

[0009] Moreover, other invention is characterized by creating an electrolyte plate, using the mixture of the ulmin acid lithium particle of an anodization mold, and the particle of the ulmin acid lithium by anodization generated \*\* as an electrolyte maintenance ingredient in said invention.

[0010] Moreover, the electrolyte plate for fused carbonate fuel cells concerning this invention is characterized by using said anodization type as an electrolyte maintenance ingredient of ulmin acid lithium particle, and the alumina fiber as a charge of substrate reinforcing materials or ulmin acid lithium fiber.

[0011] Moreover, the electrolyte plate for fused carbonate fuel cells concerning other invention is characterized by using mixture with the particle of the ulmin acid lithium by said anodization type as an electrolyte maintenance ingredient of ulmin acid lithium particle, and anodization generated \*\*, the alumina fiber as a charge of substrate reinforcing materials, or ulmin acid lithium fiber.

[0012] Moreover, the electrolyte plate for fused carbonate fuel cells concerning other invention Specific surface area by 0.05 to 0.2 micrometers by 0.05 to 1 micrometer Mixture with the ulmin acid lithium particle of 10 to 30m<sup>2</sup>/g, [ the ulmin acid lithium particle and primary particle size of an anodization mold whose specific surface area the particle size of the direction of a major axis as an electrolyte maintenance ingredient is 60m<sup>2</sup>/g from 30 ] It is characterized by using the alumina fiber as a charge of substrate reinforcing materials, or ulmin acid lithium fiber.

[0013] Moreover, the electrolyte plate for fused carbonate fuel cells concerning other invention is characterized by containing the ulmin acid lithium of an anodization mold 0.3 or more by the weight ratio to other ulmin acid lithium particles in invention of said electrolyte plate.

[0014] Moreover, it is characterized by for the fused carbonate fuel cell concerning this invention being a fused carbonate fuel cell equipped with the electrolyte plate and anode which carried out the arbitration number-of-sheets laminating, and the cathode, and said electrolyte plates being said one of electrolyte plates for fused carbonate fuel cells.

[0015]

[Embodiment of the Invention] An aluminum oxide is obtained by electrolyzing in an electrolyte

water solution by making aluminum into an anode plate. It is possible by using an acidic solution for an electrolyte water solution at this time for the oxide skin which the alternative dissolution arises and has regular pore structure during electrolysis to be obtained, and to create 1 billion or more pores per 1 square millimeter anodic oxidation aluminum (about 0.01 micrometers - 0.001 micrometers aperture) by control of formation voltage moreover. The lithiation anodization aluminum, i.e., the ulmin acid lithium of an anodization mold, whose stability over a carbonate improved by lithiating porous mold anodization aluminum with this large surface area is obtained. The specific surface area of the ulmin acid lithium particle of the anodization mold of 0.1 micrometers of mean diameters after passing through crack / classification process is 30-60m<sup>2</sup>/g, and can be increased rather than specific-surface-area of 10-30m<sup>2</sup>/g of the ulmin acid lithium particle of the diameter of said generated \*\* by the anodization currently used conventionally.

[0016] If the range of the particle size of the ulmin acid lithium particle of an anodization mold is 0.05 to 1 micrometer, it is checked that it is satisfactory about pore distribution, porosity, and electrolyte plate reinforcement. Since the irregularity which it not only holds an electrolyte by the pore between particles, but the particle itself has is the structure suitable for holding an electrolyte, the crack particle of the ulmin acid lithium of a porous anodization mold can minor-diameter-size conventionally pore formed into this electrolyte plate. Therefore, electrolyte holding power of the electrolyte plate produced using the ulmin acid lithium particle of a porous anodization mold improves. This electrolyte plate has still larger surface relief, and since it was produced using the particle with a high specific surface area, porosity can enlarge as compared with 57 to 63%, and the conventional electrolyte plate. When it uses for a cell, the improvement in the engine performance is attained for ionic conduction resistance reduction of an electrolyte plate.

[0017]

[Example] Drawing 1 is the flow chart of ulmin acid lithium particle production of the anodization mold which used the anodization aluminum of this invention as the raw material. A process 10 is an anodic oxidation process which metal aluminum 1 is electrochemically oxidized in the sulfuric-acid aqueous acids 2, and produces the aluminum oxide of porous structure. A process 11 is a clearance process to which selective dissolution of the aluminum of the substrate ingredient which remained without anodizing is carried out using the basic water solution (NaOHaq.) 3. A process 12 is a lithiation process for using as the ulmin acid lithium of an anodization mold the aluminum oxide formed of anodization using lithium salt (Li<sub>2</sub>CO<sub>3</sub>) 4. A process 13 is a crushing process which cracks the ulmin acid lithium of an anodization mold to a submicron particle. A process 14 as the ulmin acid lithium particle of the anodization mold obtained by processing to the organic compound 5 and said process 13 as a binder and a plasticizer, the other ulmin acid lithium particle 6, and an additive 7 for the improvement in substrate on the strength An alumina fiber, The production process which produces an electrolyte plate sheet from either of ulmin acid lithium fiber is expressed.

[0018] The electrolyte plate producing method concrete as an example (1) is described below. Electrolysis with constant current was performed having made into the anode plate 300 to 500 micrometers [ which performed chemical-polishing processing beforehand ] aluminum sheet metal 1, having used a metal mesh as the negative electrode, and cooling with the current density of 40 mA/cm<sup>2</sup> in the 0.1 sulfuric-acid water solution 2 of M, and 500-micrometer anodized coating was produced from 50 micrometers in thickness. Since the substrate part of the obtained anodized coating was metal aluminum, in the 1 sodium-hydroxide water solution 3 of M, it was

left for 15 hours, and dissolution clearance of the aluminum was carried out, it washed and dried, and it obtained the anodic oxidation aluminum of porous structure. This oxide was heated at 650 to 750 degrees C under air or a carbon-dioxide-gas ambient atmosphere with the lithium carbonate 4 of an amount weight ratio 5 times for 240 hours, and lithiation processing was performed. In this way, the ulmin acid lithium of the made anodization mold was cracked with the ball mill for 8 hours, it classified after that, and the path of the direction of a major axis produced the ulmin acid lithium particle of a 0.05 to 1 micrometer anodization mold.

[0019] 270g of ulmin acid lithiums 6 formed in the solution 5 of the organic compound made to dissolve polyvinyl-butylal 40ml in a mixed organic solvent (ethyl alcohol 300ml and butyl alcohol 100ml) without depending the above-mentioned process on anodization with a primary particle size of 0.1 micrometers by 115g of ulmin acid lithium particles of an anodization mold with a primary particle diameter of about 0.1 micrometers and specific-surface-area of 20m<sup>2</sup>/g pass was added, and it mixed with the ball mill for 4 hours. Then, the fiber 7 for substrate reinforcement which added 100g of 60-micrometer alumina fibers 7 to butyl alcohol 120ml from the diameter of 20 micrometers, and was cracked with the ball mill for 2 hours was added, and it mixed for further 4 hours, and considered as the electrolyte plate slurry. And after carrying out viscosity control, the electrolyte plate sheet was produced with the doctor blade method (shaping of "fine ceramics and CMC pp.219-223 written by organic material" Katsuyoshi Saito).

[0020] The method of producing a conventional-type electrolyte plate is shown below as an example of a comparison (1). With a primary particle size of 0.1 micrometers ulmin acid lithium 380g was added to the solution made to dissolve polyvinyl-butylal 40ml in a mixed organic solvent (ethyl alcohol 300ml and butyl alcohol 100ml), and it mixed with the ball mill for 4 hours. The substrate reinforcement fiber which added 100g of 60-micrometer alumina fibers 7 from the butyl alcohol 120ml and the diameter of 20 micrometers, and was cracked with the ball mill for 2 hours was added, and it mixed for further 4 hours, and considered as the slurry for electrolyte plates, and the electrolyte plate sheet was produced with the doctor blade method after viscosity control.

[0021] After heat-treating at 650 degrees C under an air ambient atmosphere for 3 hours about the example 1 which is this electrolyte plate and carrying out the pyrolysis of the organic binder, pore distribution is measured, and the result compared with the example of a comparison (1) which is a conventional type is shown in drawing 2. Porosity of an example (1) is improving about 7% from the example of a comparison (1), and most big and rough holes with a pole diameter of 1 micrometers or more do not exist. Moreover, the pore distribution within a field was almost uniform.

[0022] The effect which the weight ratio of the ulmin acid lithium particle of an anodization mold and other ulmin acid lithium particles has on electrolyte plate porosity is shown in drawing 3. When the weight ratio of the ulmin acid lithium of an anodization mold to other ulmin acid lithiums exceeded 0.3, it turned out that it is in the inclination for porosity to increase. It turned out that the porosity which exceeds 60% in the 0.3 or more range is secured. The range of 0.4-1.5 is desirable at a weight ratio.

[0023] An arbitration number-of-sheets laminating is carried out. the electrolyte plate of an example (1) and the example of a comparison (1) -- two to four sheets -- It assembles, the single cel, i.e., fused carbonate fuel cell, of basic structure which arranged the nickel system porous body anode and the nickel oxide system porous body cathode up and down. Air-carbon dioxide gas was supplied as humidification hydrogen-carbon dioxide gas and oxidizing agent gas as fuel gas, and the generation-of-electrical-energy trial was performed at the temperature of 650

degrees C, using the eutectic carbonate of lithium:potassium =62:38 (mole ratio) as an electrolyte. [0024] The result of having run continuously the cel A using the electrolyte plate of an example (1) and the cel B which used the electrolyte plate of the example of a comparison (1) under current density 150 mA/cm<sup>2</sup>, 60% of fuel utilization rates, 30% of oxidizer utilization factors, and ordinary pressure is shown in drawing 4 . In the cel A using an example (1), performance degradation is not seen to electromotive force lowering of 13mV per 1000 hours having arisen in the cel B which, as a result, used the example of a comparison (1). Also in electromotive force, the example (1) is changing highly. This is considered because the porosity of an electrolyte plate increased, and resistance fell, and electrolyte holding power improved and degradation with the passage of time became small.

[0025]

[Effect of the Invention] Since, as for the electrolyte plate for fused carbonate fuel cells of this invention, the particle size of the direction of a major axis is using 0.05 to 1 micrometer lithiation anodic oxidation aluminum for a constituent particle, \*\*\*\*\* of the electrolyte under cell operation can be lessened and the initial engine performance of a cell can be maintained for a long period of time. Moreover, since high porosity is more possible than the conventional electrolyte plate, a cell with the high engine performance with low internal resistance is realizable.

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## TECHNICAL FIELD

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[Field of the Invention] This invention relates to a fuel cell, especially relates to the manufacture approach, the electrolyte plate for fused carbonate fuel cells, and fused carbonate fuel cell of the electrolyte plate for fused carbonate fuel cells.

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## PRIOR ART

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[Description of the Prior Art] The fused carbonate fuel cell forms the cell single cel by using the separator for dividing the cell which adjoins at the time of a collecting electrode plate, the passage formation wavelike plate of fuel gas and oxidant gas, and a laminating on the basis of the structure which arranged the cathode which uses as a principal component the anode which uses nickel as a principal component up and down and nickel oxide of the ulmin acid lithium porous body which is made to carry out impregnation of the melting alkali-metal carbonate, and uses it.

[0003] An electrolyte plate prevents the cross of fuel gas and oxidant gas, or leak out of a cell while insulating a positive electrode and a negative electrode electrically, and it has the role which holds the fused electrolyte of an ion conductor in a substrate further. In order to fulfill such conditions, the porosity substrate which consisted of submicron ulmin acid lithium particles is used. Moreover, in order not to check the ionic conduction of a melting carbonate, it is supposed that it is required to use an electrolyte plate as much as possible with big porosity.

[0004] The improvement proposal which raises electrolyte retention volume is made changing ceramic particle size and decreasing electrolyte dissipation to the polar zone to such a problem, with the electrolyte plate which touches the electrode of the inside which carries out two or more sheet laminating, and other electrolyte plates. There is JP,63-284764,A as the example.

Moreover, the mean particle diameter within a field is changed and it is proposed by JP,4-

286868,A about the electrolyte plate which gas-seal nature was raised and heightened electrolyte maintenance capacity.

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## EFFECT OF THE INVENTION

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[Effect of the Invention] Since, as for the electrolyte plate for fused carbonate fuel cells of this invention, the particle size of the direction of a major axis is using 0.05 to 1 micrometer lithiation anodic oxidation aluminum for a constituent particle, \*\*\*\*\* of the electrolyte under cell operation can be lessened and the initial engine performance of a cell can be maintained for a long period of time. Moreover, since high porosity is more possible than the conventional electrolyte plate, a cell with the high engine performance with low internal resistance is realizable.

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## TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] However, there is a possibility that a fused electrolyte may localize that the pore distribution in an electrolyte plate is uneven. Moreover, at a part with a large pore diameter, since relative capillary force becomes weaker, electrolyte abundance runs short, and there is also a possibility that ionic conduction resistance may increase. Furthermore, partial creep deformation of an electrolyte plate had also become a problem.

[0006] The electrolyte held at the electrolyte plate of a fused carbonate fuel cell is the generation reaction of creepage, evaporation, or a high resistance corrosion layer etc., and decrease in number with operation-time progress. The reduction in electrolytic causes the increment in ionic conduction resistance, and causes cell performance degradation. For this reason, electrolyte holding power is high and an electrolyte plate with the uniform pore distribution within a field in which big and rough pore 1 micrometers or more does not exist is required.

[0007] In order to solve such a technical problem, this invention can hold many electrolytes, and when the resistance to ionic conduction forms pore [ that it is uniform and minor diameter ] small, it uses the manufacture approach, the electrolyte plate for fused carbonate fuel cells, and fused carbonate fuel cell of the high electrolyte plate for fused carbonate fuel cells of electrolyte holding power as an offer plug.

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## MEANS

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[Means for Solving the Problem] The manufacture approach of the electrolyte plate for fused carbonate fuel cells built over this invention in order to solve such a technical problem The anodic oxidation aluminum which carries out anodic oxidation of the metal aluminum substrate electrochemically in aqueous acids, and has pore is formed. Carry out selective dissolution of the aluminum of the substrate ingredient which remained without oxidizing, remove, and it leaves porous anodic oxidation aluminum. Lithiate this anodization aluminum and it considers as the ulmin acid lithium of an anodization mold. This anodization type of ulmin acid lithium is cracked to a submicron particle, the ulmin acid lithium particle of an anodization mold is formed, and it is characterized by creating an electrolyte plate, using this anodization type of ulmin acid lithium particle as an electrolyte maintenance ingredient.

[0009] Moreover, other invention is characterized by creating an electrolyte plate, using the mixture of the ulmin acid lithium particle of an anodization mold, and the particle of the ulmin

acid lithium by anodization generated \*\* as an electrolyte maintenance ingredient in said invention.

[0010] Moreover, the electrolyte plate for fused carbonate fuel cells concerning this invention is characterized by using said anodization type as an electrolyte maintenance ingredient of ulmin acid lithium particle, and the alumina fiber as a charge of substrate reinforcing materials or ulmin acid lithium fiber.

[0011] Moreover, the electrolyte plate for fused carbonate fuel cells concerning other invention is characterized by using mixture with the particle of the ulmin acid lithium by said anodization type as an electrolyte maintenance ingredient of ulmin acid lithium particle, and anodization generated \*\*, the alumina fiber as a charge of substrate reinforcing materials, or ulmin acid lithium fiber.

[0012] Moreover, the electrolyte plate for fused carbonate fuel cells concerning other invention Specific surface area by 0.05 to 0.2 micrometers by 0.05 to 1 micrometer Mixture with the ulmin acid lithium particle of 10 to 30m<sup>2</sup>/g, [ the ulmin acid lithium particle and primary particle size of an anodization mold whose specific surface area the particle size of the direction of a major axis as an electrolyte maintenance ingredient is 60m<sup>2</sup>/g from 30 ] It is characterized by using the alumina fiber as a charge of substrate reinforcing materials, or ulmin acid lithium fiber.

[0013] Moreover, the electrolyte plate for fused carbonate fuel cells concerning other invention is characterized by containing the ulmin acid lithium of an anodization mold 0.3 or more by the weight ratio to other ulmin acid lithium particles in invention of said electrolyte plate.

[0014] Moreover, it is characterized by for the fused carbonate fuel cell concerning this invention being a fused carbonate fuel cell equipped with the electrolyte plate and anode which carried out the arbitration number-of-sheets laminating, and the cathode, and said electrolyte plates being said one of electrolyte plates for fused carbonate fuel cells.

[0015]

[Embodiment of the Invention] An aluminum oxide is obtained by electrolyzing in an electrolyte water solution by making aluminum into an anode plate. It is possible by using an acidic solution for an electrolyte water solution at this time for the oxide skin which the alternative dissolution arises and has regular pore structure during electrolysis to be obtained, and to create 1 billion or more pores per 1 square millimeter anodic oxidation aluminum (about 0.01 micrometers - 0.001 micrometers aperture) by control of formation voltage moreover. The lithiation anodization aluminum, i.e., the ulmin acid lithium of an anodization mold, whose stability over a carbonate improved by lithiating porous mold anodization aluminum with this large surface area is obtained. The specific surface area of the ulmin acid lithium particle of the anodization mold of 0.1 micrometers of mean diameters after passing through crack / classification process is 30-60m<sup>2</sup>/g, and can be increased rather than specific-surface-area of 10-30m<sup>2</sup>/g of the ulmin acid lithium particle of the diameter of said generated \*\* by the anodization currently used conventionally.

[0016] If the range of the particle size of the ulmin acid lithium particle of an anodization mold is 0.05 to 1 micrometer, it is checked that it is satisfactory about pore distribution, porosity, and electrolyte plate reinforcement. Since the irregularity which it not only holds an electrolyte by the pore between particles, but the particle itself has is the structure suitable for holding an electrolyte, the crack particle of the ulmin acid lithium of a porous anodization mold can minor-diameter-size conventionally pore formed into this electrolyte plate. Therefore, electrolyte holding power of the electrolyte plate produced using the ulmin acid lithium particle of a porous anodization mold improves. This electrolyte plate has still larger surface relief, and since it was



produced using the particle with a high specific surface area, porosity can enlarge as compared with 57 to 63%, and the conventional electrolyte plate. When it uses for a cell, the improvement in the engine performance is attained for ionic conduction resistance reduction of an electrolyte plate.

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## EXAMPLE

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[Example] Drawing 1 is the flow chart of ulmin acid lithium particle production of the anodization mold which used the anodization aluminum of this invention as the raw material. A process 10 is an anodic oxidation process which metal aluminum 1 is electrochemically oxidized in the sulfuric-acid aqueous acids 2, and produces the aluminum oxide of porous structure. A process 11 is a clearance process to which selective dissolution of the aluminum of the substrate ingredient which remained without anodizing is carried out using the basic water solution (NaOHaq.) 3. A process 12 is a lithiation process for using as the ulmin acid lithium of an anodization mold the aluminum oxide formed of anodization using lithium salt ( $\text{Li}_2\text{CO}_3$ ) 4. A process 13 is a crushing process which cracks the ulmin acid lithium of an anodization mold to a submicron particle. A process 14 as the ulmin acid lithium particle of the anodization mold obtained by processing to the organic compound 5 and said process 13 as a binder and a plasticizer, the other ulmin acid lithium particle 6, and an additive 7 for the improvement in substrate on the strength An alumina fiber, The production process which produces an electrolyte plate sheet from either of ulmin acid lithium fiber is expressed.

[0018] The electrolyte plate producing method concrete as an example (1) is described below. Electrolysis with constant current was performed having made into the anode plate 300 to 500 micrometers [ which performed chemical-polishing processing beforehand ] aluminum sheet metal 1, having used a metal mesh as the negative electrode, and cooling with the current density of 40 mA/cm<sup>2</sup> in the 0.1 sulfuric-acid water solution 2 of M, and 500-micrometer anodized coating was produced from 50 micrometers in thickness. Since the substrate part of the obtained anodized coating was metal aluminum, in the 1 sodium-hydroxide water solution 3 of M, it was left for 15 hours, and dissolution clearance of the aluminum was carried out, it washed and dried, and it obtained the anodic oxidation aluminum of porous structure. This oxide was heated at 650 to 750 degrees C under air or a carbon-dioxide-gas ambient atmosphere with the lithium carbonate 4 of an amount weight ratio 5 times for 240 hours, and lithiation processing was performed. In this way, the ulmin acid lithium of the made anodization mold was cracked with the ball mill for 8 hours, it classified after that, and the path of the direction of a major axis produced the ulmin acid lithium particle of a 0.05 to 1 micrometer anodization mold.

[0019] 270g of ulmin acid lithiums 6 formed in the solution 5 of the organic compound made to dissolve polyvinyl-butyril 40ml in a mixed organic solvent (ethyl alcohol 300ml and butyl alcohol 100ml) without depending the above-mentioned process on anodization with a primary particle size of 0.1 micrometers by 115g of ulmin acid lithium particles of an anodization mold with a primary particle diameter of about 0.1 micrometers and specific-surface-area of 20m<sup>2</sup>/g pass was added, and it mixed with the ball mill for 4 hours. Then, the fiber 7 for substrate reinforcement which added 100g of 60-micrometer alumina fibers 7 to butyl alcohol 120ml from the diameter of 20 micrometers, and was cracked with the ball mill for 2 hours was added, and it mixed for further 4 hours, and considered as the electrolyte plate slurry. And after carrying out viscosity control, the electrolyte plate sheet was produced with the doctor blade method (shaping of "fine ceramics and CMC pp.219-223 written by organic material" Katsuyoshi Saito).

[0020] The method of producing a conventional-type electrolyte plate is shown below as an example of a comparison (1). With a primary particle size of 0.1 micrometers ulmin acid lithium 380g was added to the solution made to dissolve polyvinyl-butyral 40ml in a mixed organic solvent (ethyl alcohol 300ml and butyl alcohol 100ml), and it mixed with the ball mill for 4 hours. The substrate reinforcement fiber which added 100g of 60-micrometer alumina fibers 7 from the butyl alcohol 120ml and the diameter of 20 micrometers, and was cracked with the ball mill for 2 hours was added, and it mixed for further 4 hours, and considered as the slurry for electrolyte plates, and the electrolyte plate sheet was produced with the doctor blade method after viscosity control.

[0021] After heat-treating at 650 degrees C under an air ambient atmosphere for 3 hours about the example 1 which is this electrolyte plate and carrying out the pyrolysis of the organic binder, pore distribution is measured, and the result compared with the example of a comparison (1) which is a conventional type is shown in drawing 2 . Porosity of an example (1) is improving about 7% from the example of a comparison (1), and most big and rough holes with a pole diameter of 1 micrometers or more do not exist. Moreover, the pore distribution within a field was almost uniform.

[0022] The effect which the weight ratio of the ulmin acid lithium particle of an anodization mold and other ulmin acid lithium particles has on electrolyte plate porosity is shown in drawing 3 . When the weight ratio of the ulmin acid lithium of an anodization mold to other ulmin acid lithiums exceeded 0.3, it turned out that it is in the inclination for porosity to increase. It turned out that the porosity which exceeds 60% in the 0.3 or more range is secured. The range of 0.4-1.5 is desirable at a weight ratio.

[0023] An arbitration number-of-sheets laminating is carried out. the electrolyte plate of an example (1) and the example of a comparison (1) -- two to four sheets -- It assembles, the single cel, i.e., fused carbonate fuel cell, of basic structure which arranged the nickel system porous body anode and the nickel oxide system porous body cathode up and down. Air-carbon dioxide gas was supplied as humidification hydrogen-carbon dioxide gas and oxidizing agent gas as fuel gas, and the generation-of-electrical-energy trial was performed at the temperature of 650 degrees C, using the eutectic carbonate of lithium:potassium =62:38 (mole ratio) as an electrolyte.

[0024] The result of having run continuously the cel A using the electrolyte plate of an example (1) and the cel B which used the electrolyte plate of the example of a comparison (1) under current density 150 mA/cm<sup>2</sup>, 60% of fuel utilization rates, 30% of oxidizer utilization factors, and ordinary pressure is shown in drawing 4 . In the cel A using an example (1), performance degradation is not seen to electromotive force lowering of 13mV per 1000 hours having arisen in the cel B which, as a result, used the example of a comparison (1). Also in electromotive force, the example (1) is changing highly. This is considered because the porosity of an electrolyte plate increased, and resistance fell, and electrolyte holding power improved and degradation with the passage of time became small.

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## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is process drawing showing the manufacture flow of the electrolyte plate for fused carbonate fuel cells of this invention.

[Drawing 2] It is a pore distribution map after debinder baking of the electrolyte plate for fused carbonate fuel cells of this invention, and a conventional-type electrolyte plate.

[Drawing 3] It is the graph which shows the weight ratio of an anodization mold ulmin acid lithium to an ulmin acid lithium, and the relation of electrolyte plate porosity.

[Drawing 4] It is the graph which shows an engine-performance change of the fused carbonate fuel cell using the electrolyte plate of this invention and the conventional electrolyte plate with the passage of time.

[Description of Notations]

- 1 Aluminum
- 2 0.1M Sulfuric-Acid Water Solution
- 3 1M Sodium-Hydroxide Water Solution
- 4 Lithium Carbonate
- 5 Organic Compound
- 6 Ulmin Acid Lithium
- 7 Reinforcement Fiber
- 10 Anodic Oxidation Process
- 11 Aluminum Clearance Process
- 12 Lithiation Process
- 13 Crushing Process
- 14 Electrolyte Sheet Production Process

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## CLAIMS

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[Claim(s)]

[Claim 1] The anodic oxidation aluminum which carries out anodic oxidation of the metal aluminum substrate electrochemically in aqueous acids, and has pore is formed. Carry out selective dissolution of the aluminum of the substrate ingredient which remained without oxidizing, remove, and it leaves porous anodic oxidation aluminum. Lithiate this anodization aluminum and it considers as the ulmin acid lithium of an anodization mold. Crack this anodization type of ulmin acid lithium to a submicron particle, and the ulmin acid lithium particle of an anodization mold is formed. The manufacture approach of the electrolyte plate for fused carbonate fuel cells characterized by creating an electrolyte plate, using this anodization type of ulmin acid lithium particle as an electrolyte maintenance ingredient.

[Claim 2] The manufacture approach of the electrolyte plate for fused carbonate fuel cells characterized by creating an electrolyte plate in claim 1, using the mixture of the ulmin acid lithium particle of an anodization mold, and the particle of the ulmin acid lithium by anodization generated \*\* as an electrolyte maintenance ingredient.

[Claim 3] The electrolyte plate for fused carbonate fuel cells characterized by using the anodization type according to claim 1 as an electrolyte maintenance ingredient of ulmin acid lithium particle, and the alumina fiber as a charge of substrate reinforcing materials or ulmin acid lithium fiber.

[Claim 4] The electrolyte plate for fused carbonate fuel cells characterized by using mixture with the particle of the ulmin acid lithium by the anodization type according to claim 1 as an electrolyte maintenance ingredient of ulmin acid lithium particle, and anodization generated \*\*, the alumina fiber as a charge of substrate reinforcing materials, or ulmin acid lithium fiber.

[Claim 5] The electrolyte plate for fused carbonate fuel cells with which specific surface area is characterized by mixture with the ulmin acid lithium particle of 10 to 30m<sup>2</sup>/g, and using the alumina fiber as a charge of substrate reinforcing materials, or ulmin acid lithium fiber by 0.05 to

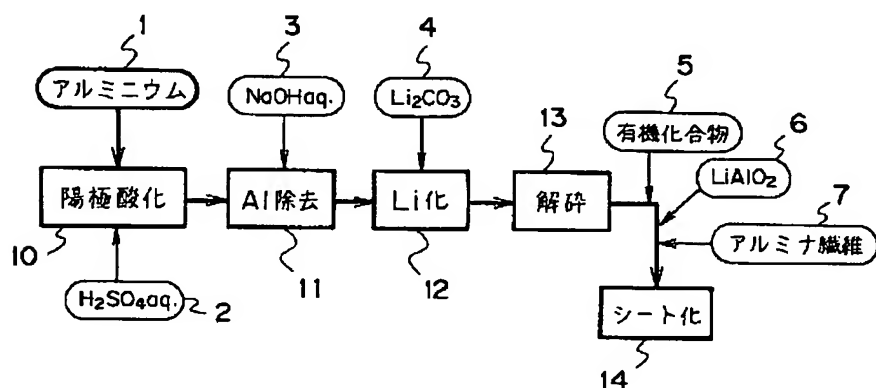
0.2 micrometers by the ulmin acid lithium particle and primary particle size of an anodization mold whose specific surface area the particle size of the direction of a major axis as an electrolyte maintenance ingredient is 60m<sup>2</sup>/g from 30 in 0.05 to 1 micrometer.

[Claim 6] The electrolyte plate for fused carbonate fuel cells characterized by containing the ulmin acid lithium of an anodization mold 0.3 or more by the weight ratio to other ulmin acid lithium particles in claim 4 or 5.

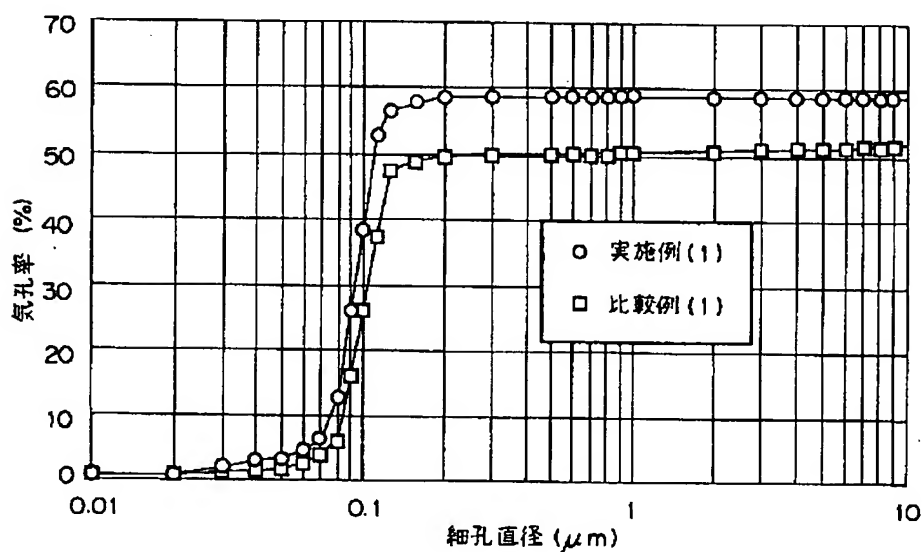
[Claim 7] It is the fused carbonate fuel cell characterized by said electrolyte plate being an electrolyte plate for fused carbonate fuel cells according to claim 3 to 6 in the fused carbonate fuel cell equipped with the electrolyte plate and anode which carried out the arbitration number-of-sheets laminating, and the cathode.

## DRAWINGS

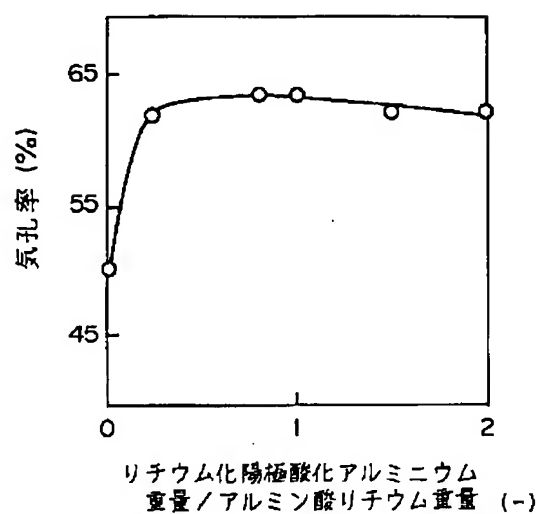
[Drawing 1]



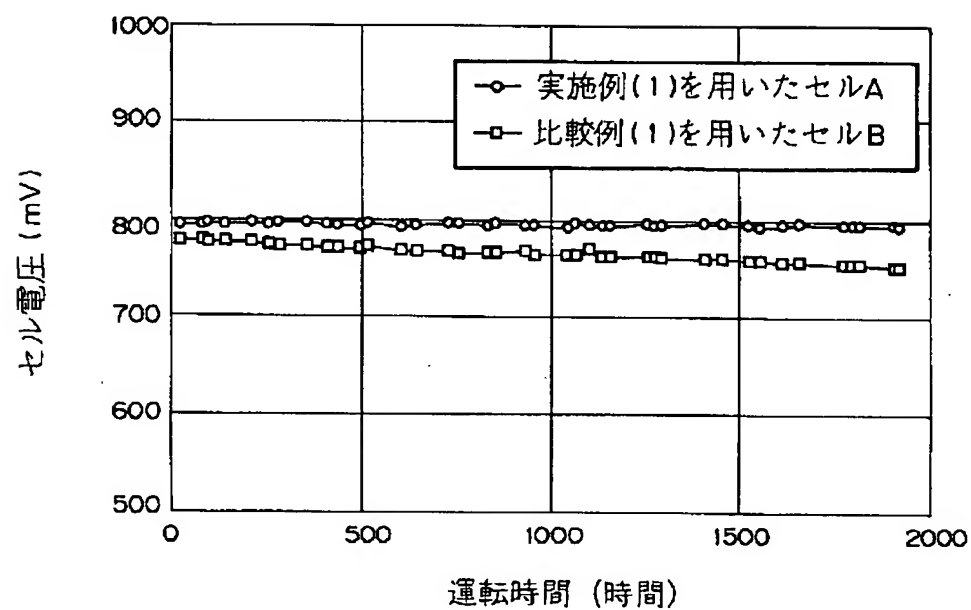
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Translation done.]

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溶融炭酸塩型燃料電池発電システム技術研  
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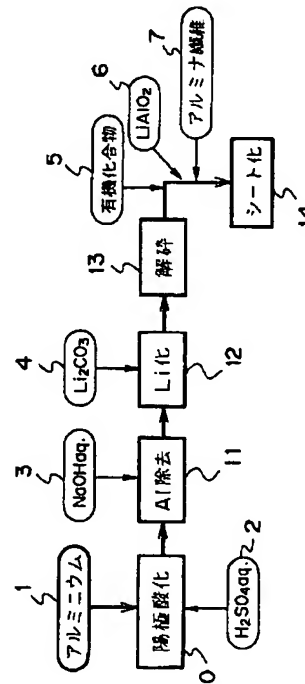
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(54) 【発明の名称】 溶融炭酸塩型燃料電池用電解質板の製造方法及び溶融炭酸塩型燃料電池用電解質板

(57) 【要約】 (修正有)

【解決手段】 アルミニウムを酸性水溶液中で電気化学的にアノード酸化した陽極酸化アルミニウムをリチウム化後0.05  $\mu\text{m}$ から1  $\mu\text{m}$ に解砕した比表面積の大きな粒子を電解質保持材料に用いて電解質板を形成する。

【効果】 電解質保持材料に比表面積の大きな陽極酸化型アルミン酸リチウムを使用しているので、電解質を多く保持することが出来、かつイオン伝導に対する抵抗が小さく、また均一で小径な細孔を形成することにより電解質保持力の高い電質板とすることができる。



## 【特許請求の範囲】

【請求項1】 金属アルミニウム基板を酸性水溶液中で電気化学的にアノード酸化して細孔を有する陽極酸化アルミニウムを形成し、酸化されずに残った基板材料のアルミニウムを選択溶解させて除去して多孔質の陽極酸化アルミニウムを残し、この陽極酸化アルミニウムをリチウム化して陽極酸化型のアルミン酸リチウムとし、この陽極酸化型のアルミン酸リチウムをサブミクロンの粒子に解砕して陽極酸化型のアルミン酸リチウム粒子を形成し、この陽極酸化型のアルミン酸リチウム粒子を電解質保持材料として用いて電解質板を作成することを特徴とする熔融炭酸塩型燃料電池用電解質板の製造方法。

【請求項2】 請求項1において、陽極酸化型のアルミン酸リチウム粒子と陽極酸化によらずに生成されたアルミン酸リチウムの粒子との混合物を電解質保持材料として用いて電解質板を作成することを特徴とする熔融炭酸塩型燃料電池用電解質板の製造方法。

【請求項3】 電解質保持材料としての請求項1に記載の陽極酸化型のアルミン酸リチウム粒子と、基板補強材料としてのアルミナ繊維あるいはアルミン酸リチウム繊維とを用いたことを特徴とする熔融炭酸塩型燃料電池用電解質板。

【請求項4】 電解質保持材料としての請求項1に記載の陽極酸化型のアルミン酸リチウム粒子及び陽極酸化によらずに生成されたアルミン酸リチウムの粒子との混合物と、基板補強材料としてのアルミナ繊維あるいはアルミン酸リチウム繊維とを用いたことを特徴とする熔融炭酸塩型燃料電池用電解質板。

【請求項5】 電解質保持材料としての長軸方向の粒径が $0.05\mu\text{m}$ から $1\mu\text{m}$ で比表面積が $30$ から $60\text{m}^2/\text{g}$ である陽極酸化型のアルミン酸リチウム粒子及び一次粒径が $0.05\mu\text{m}$ から $0.2\mu\text{m}$ で比表面積が $10$ から $30\text{m}^2/\text{g}$ のアルミン酸リチウム粒子との混合物と、基板補強材料としてのアルミナ繊維あるいはアルミン酸リチウム繊維を用いたことを特徴とする熔融炭酸塩型燃料電池用電解質板。

【請求項6】 請求項4又は5において、陽極酸化型のアルミン酸リチウムが他のアルミン酸リチウム粒子に対し重量比で $0.3$ 以上含まれていることを特徴とする熔融炭酸塩型燃料電池用電解質板。

【請求項7】 任意枚数積層した電解質板とアノードとカソードを備えた熔融炭酸塩型燃料電池において、前記電解質板は請求項3～6のいずれかに記載の熔融炭酸塩型燃料電池用電解質板であることを特徴とする熔融炭酸塩型燃料電池。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、燃料電池に係り、特に熔融炭酸塩型燃料電池用電解質板の製造方法、熔融炭酸塩型燃料電池用電解質板及び熔融炭酸塩型燃料電池

に関するものである。

## 【0002】

【従来の技術】熔融炭酸塩型燃料電池は、熔融アルカリ金属炭酸塩を含浸させて用いるアルミン酸リチウム多孔質体の上下にニッケルを主成分とするアノードと酸化ニッケルを主成分とするカソードを配した構造を基本とし、その他集電板、燃料ガス・酸化剤ガスの流路形成波状板、積層時に隣接する電池を分割するためのセパレータを用いることで電池単セルを形成している。

【0003】電解質板は、正極と負極を電氣的に絶縁するとともに燃料ガス・酸化剤ガスのクロスあるいは電池外へのリークを防止し、さらにイオン伝導体の熔融電解質を基板中に保持する役割を持つ。このような条件を満たすためにサブミクロンのアルミン酸リチウム粒子で構成された多孔質基板が使用されている。また熔融炭酸塩のイオン伝導を阻害しないためにはできるだけ気孔率の大きな電解質板を用いることが必要であるとされている。

【0004】このような問題に対し、複数枚積層するうちの電極に接する電解質板とその他の電解質板で、セラミック粒径を変化させ電極部への電解質散逸を減少させつつ電解質保持容量を高める改善提案がなされている。その例として特開昭63-284764号公報がある。また面内の平均粒径を変化させ、ガスシール性を向上させ電解質保持能力を高めた電解質板については特開平4-286868号公報で提案されている。

## 【0005】

【発明が解決しようとする課題】しかし、電解質板中の細孔分布が不均一であると、熔融電解質が局在化する恐れがある。また細孔径が大きい部所では相対的な毛管力が弱まるため電解質存在量が不足し、イオン伝導抵抗が増加する恐れもある。さらに電解質板の部分的なクリープ変形も問題となっていた。

【0006】熔融炭酸塩型燃料電池の電解質板に保持される電解質は、クリーページ、蒸発、あるいは高抵抗腐食層の生成反応等で、運転時間経過にともなって減少する。電解質の減少はイオン伝導抵抗増加を引き起こし電池性能劣化の原因となる。このため電解質保持力が高く、かつ $1\mu\text{m}$ 以上の粗大な細孔が存在しない、面内細孔分布が均一な電解質板が必要である。

【0007】本発明は、このような課題を解決するために、電解質を多く保持することが出来、かつイオン伝導に対する抵抗が小さく、また均一で小径な細孔を形成することにより電解質保持力の高い熔融炭酸塩型燃料電池用電解質板の製造方法、熔融炭酸塩型燃料電池用電解質板及び熔融炭酸塩型燃料電池を提供せんとするものである。

## 【0008】

【課題を解決するための手段】このような課題を解決するために本発明に係る熔融炭酸塩型燃料電池用電解質板

の製造方法は、金属アルミニウム基板を酸性水溶液中で電気化学的にアノード酸化して細孔を有する陽極酸化アルミニウムを形成し、酸化されずに残った基板材料のアルミニウムを選択溶解させて除去して多孔質の陽極酸化アルミニウムを残し、この陽極酸化アルミニウムをリチウム化して陽極酸化型のアルミン酸リチウムとし、この陽極酸化型のアルミン酸リチウムをサブミクロンの粒子に解砕して陽極酸化型のアルミン酸リチウム粒子を形成し、この陽極酸化型のアルミン酸リチウム粒子を電解質保持材料として用いて電解質板を作成することを特徴とするものである。

【0009】また他の発明は、前記発明において、陽極酸化型のアルミン酸リチウム粒子と陽極酸化によらずに生成されたアルミン酸リチウムの粒子との混合物を電解質保持材料として用いて電解質板を作成することを特徴とするものである。

【0010】また本発明に係る熔融炭酸塩型燃料電池用電解質板は、電解質保持材料としての前記陽極酸化型のアルミン酸リチウム粒子と、基板補強材料としてのアルミナ繊維あるいはアルミン酸リチウム繊維とを用いたこと

を特徴とするものである。

【0011】また他の発明に係る熔融炭酸塩型燃料電池用電解質板は、電解質保持材料としての前記陽極酸化型のアルミン酸リチウム粒子及び陽極酸化によらずに生成されたアルミン酸リチウムの粒子との混合物と、基板補強材料としてのアルミナ繊維あるいはアルミン酸リチウム繊維とを用いたことを特徴とするものである。

【0012】また他の発明に係る熔融炭酸塩型燃料電池用電解質板は、電解質保持材料としての長軸方向の粒径が $0.05\mu\text{m}$ から $1\mu\text{m}$ で比表面積が $30$ から $60\text{m}^2/\text{g}$ である陽極酸化型のアルミン酸リチウム粒子及び一次粒径が $0.05\mu\text{m}$ から $0.2\mu\text{m}$ で比表面積が $10$ から $30\text{m}^2/\text{g}$ のアルミン酸リチウム粒子との混合物と、基板補強材料としてのアルミナ繊維あるいはアルミン酸リチウム繊維を用いたことを特徴とするものである。

【0013】また他の発明に係る熔融炭酸塩型燃料電池用電解質板は、前記電解質板の発明において、陽極酸化型のアルミン酸リチウムが他のアルミン酸リチウム粒子に対し重量比で $0.3$ 以上含まれていることを特徴とするものである。

【0014】また本発明に係る熔融炭酸塩型燃料電池は、任意枚数積層した電解質板とアノードとカソードを備えた熔融炭酸塩型燃料電池であって、前記電解質板は前記いずれかの熔融炭酸塩型燃料電池用電解質板であることを特徴とするものである。

【0015】

【発明の実施の形態】アルミニウムを陽極として電解質水溶液中で電気分解することにより酸化アルミニウムが得られる。このとき電解質水溶液に酸性溶液を用いるこ

とにより電気分解中に選択的な溶解が生じて規則的な細孔構造をもつ酸化被膜が得られ、しかも化成電圧の制御により陽極酸化アルミニウム $1$ 平方ミリメートル当たり $10$ 億個以上の細孔(約 $0.01\mu\text{m}$ ～ $0.001\mu\text{m}$ の孔径)を作成することが可能である。この表面積の大きいポーラス型陽極酸化アルミニウムをリチウム化することで炭酸塩に対する安定性が向上したりリチウム化陽極酸化アルミニウムすなわち陽極酸化型のアルミン酸リチウムが得られる。解砕・分級過程を経た後の平均粒径 $0.1\mu\text{m}$ の陽極酸化型のアルミン酸リチウム粒子の比表面積は $30\sim60\text{m}^2/\text{g}$ であり、従来使用されている陽極酸化によらずに生成された同径のアルミン酸リチウム粒子の比表面積 $10\sim30\text{m}^2/\text{g}$ よりも増大させることができる。

【0016】陽極酸化型のアルミン酸リチウム粒子の粒径は $0.05\mu\text{m}$ から $1\mu\text{m}$ の範囲であれば、細孔分布や気孔率、電解質板強度に問題はないことが確認されている。多孔質の陽極酸化型のアルミン酸リチウムの解砕粒子は粒子間細孔で電解質を保持するのみでなく粒子自身のもつ凹凸が電解質を保持するのに適した構造であるため該電解質板中に形成される細孔を従来よりも小径化することができる。よって多孔質の陽極酸化型のアルミン酸リチウム粒子を用いて作製された電解質板は電解質保持力が向上する。さらに該電解質板は表面起伏が大きく、比表面積の高い粒子を用いて作製されたので気孔率が $57\%$ から $63\%$ と従来の電解質板に比較し大きくすることができる。電池に用いたときには電解質板のイオン伝導抵抗減少のため、性能向上が可能となる。

【0017】

【実施例】図1は本発明の陽極酸化アルミニウムを原料とした陽極酸化型のアルミン酸リチウム粒子作製の流れ図である。工程10は金属アルミニウム1を硫酸酸性水溶液2中で電気化学的に酸化させてポーラス構造の酸化アルミニウムを作製する陽極酸化工程であり、工程11は陽極酸化されずに残った基板材料のアルミニウムを塩基性水溶液( $\text{NaOH aq.}$ )3を用いて選択溶解させる除去工程であり、工程12は陽極酸化により形成された酸化アルミニウムをリチウム塩( $\text{Li}_2\text{CO}_3$ )4を用いて陽極酸化型のアルミン酸リチウムとするためのリチウム化工程であり、工程13は陽極酸化型のアルミン酸リチウムをサブミクロンの粒子に解砕する解砕工程であり、工程14は結合剤、可塑剤としての有機化合物5と前記工程13までの処理によって得られた陽極酸化型のアルミン酸リチウム粒子とそれ以外のアルミン酸リチウム粒子6と基板強度向上のための添加物7としてアルミナ繊維、アルミン酸リチウム繊維のいずれかから電解質板シートを作製する製造工程を表している。

【0018】以下に実施例(1)として具体的な電解質板作製法を述べる。あらかじめ化学研磨処理を施した $300\mu\text{m}$ から $500\mu\text{m}$ のアルミニウム薄板1を陽極と



し、金属メッシュを負極にして0.1Mの硫酸水溶液2中で40mA/cm<sup>2</sup>の電流密度で冷却しながら定電流電解を行い、厚さ50μmから500μmの陽極酸化被膜を作製した。得られた陽極酸化被膜の基板部分は金属アルミニウムであるため1Mの水酸化ナトリウム水溶液3中に15時間放置してアルミニウムを溶解除去し、洗浄・乾燥してポーラス構造の陽極酸化アルミニウムを得た。この酸化物を重量比5倍量の炭酸リチウム4とともにに空気あるいは炭酸ガス雰囲気下650℃から750℃で240時間加熱してリチウム処理を行った。こうしてできた陽極酸化型のアルミン酸リチウムをボールミルで8時間解砕しその後分級し、長軸方向の径が0.05μmから1μmの陽極酸化型のアルミン酸リチウム粒子を作製した。

【0019】エチルアルコール300ml、ブチルアルコール100mlの混合有機溶媒にポリビニルブチラール40mlを溶解させた有機化合物の溶液5に、上記の工程を経て得られた一次粒子径約0.1μmの陽極酸化型のアルミン酸リチウム粒子115gと比表面積20m<sup>2</sup>/gで一次粒径0.1μmの陽極酸化によらないで形成されたアルミン酸リチウム6を270g加え、ボールミルで4時間混合した。その後、ブチルアルコール120mlに直径20μmから60μmのアルミナ繊維7を100g加えてボールミルで2時間解砕した基板補強用繊維7を加えてさらに4時間混合して電解質板スラリーとした。そして粘度調整した後ドクターブレード法（「フラインセラムミックスの成形と有機材料」 斎藤勝義著 シーエムシー pp.219～223）により電解質板シートを作製した。

【0020】比較例（1）として従来型電解質板の作製法を以下に示す。エチルアルコール300ml、ブチルアルコール100mlの混合有機溶媒にポリビニルブチラール40mlを溶解させた溶液に、一次粒径0.1μmのアルミン酸リチウム380gを加えボールミルで4時間混合した。そのブチルアルコール120mlと直径20μmから60μmのアルミナ繊維7を100g加えてボールミルで2時間解砕した基板補強繊維を加えてさらに4時間混合して電解質板用スラリーとし、粘度調整後ドクターブレード法により電解質板シートを作製した。

【0021】該電解質板である実施例1について空気雰囲気下650℃で3時間熱処理し有機バインダを熱分解させた後細孔分布を測定し、従来型である比較例（1）と比較した結果を図2に示す。実施例（1）は比較例（1）よりも気孔率が7%程度向上しており、細孔径1μm以上の粗大空孔はほとんど存在していない。また面内の細孔分布はほぼ均一であった。

【0022】陽極酸化型のアルミン酸リチウム粒子と他のアルミン酸リチウム粒子の重量比が電解質板気孔率に与える影響を図3に示す。他のアルミン酸リチウムに対

する陽極酸化型のアルミン酸リチウムの重量比が0.3を上回ると気孔率が增大する傾向にあることが判った。0.3以上の範囲で60%を超える気孔率を確保していることが判った。重量比で0.4～1.5の範囲が好ましい。

【0023】実施例（1）と比較例（1）の電解質板を2枚から4枚の任意枚数積層し、その上下にニッケル系多孔質体アノードと酸化ニッケル系多孔質体カソードを配した基本構造の単セルすなわち溶融炭酸塩型燃料電池を組み立て、燃料ガスとして加湿水素-炭酸ガス、酸化剤ガスとして空気-炭酸ガスを供給し、電解質としてリチウム：カリウム=62：38（モル比）の共晶炭酸塩を用いて、温度650℃で発電試験を行った。

【0024】実施例（1）の電解質板を用いたセルAと比較例（1）の電解質板を使用したセルBを電流密度150mA/cm<sup>2</sup>、燃料利用率60%、酸化剤利用率30%、常圧下で連続運転した結果を図4に示す。その結果比較例（1）を使用したセルBでは1000時間あたり13mVの起電力低下が生じたのに対し、実施例（1）を用いたセルAでは性能劣化はみられない。起電力も実施例（1）が高く推移している。これは電解質板の気孔率が増加して抵抗が下がり、かつ電解質保持力が向上し経時劣化が小さくなったためと考えられる。

【0025】

【発明の効果】本発明の溶融炭酸塩型燃料電池用電解質板は構成粒子に長軸方向の粒径が0.05μmから1μmのリチウム化陽極酸化アルミニウムを使用しているので、電池運転中における電解質の損逸量を少なくすることができ電池初期性能を長期間維持できる。また従来の電解質板よりも高気孔率が可能なため、内部抵抗の低く性能の高い電池を実現できる。

【図面の簡単な説明】

【図1】本発明の溶融炭酸塩型燃料電池用電解質板の製造フローを示す工程図である。

【図2】本発明の溶融炭酸塩型燃料電池用電解質板と従来型電解質板の脱バインダ焼成後の細孔分布図である。

【図3】アルミン酸リチウムに対する陽極酸化型アルミン酸リチウムの重量比と電解質板気孔率の関係を示すグラフである。

【図4】本発明の電解質板と従来の電解質板を用いた溶融炭酸塩型燃料電池の経時性能変化を示すグラフである。

【符号の説明】

- 1 アルミニウム
- 2 0.1M硫酸水溶液
- 3 1M水酸化ナトリウム水溶液
- 4 炭酸リチウム
- 5 有機化合物
- 6 アルミン酸リチウム
- 7 補強繊維

10 陽極酸化工程

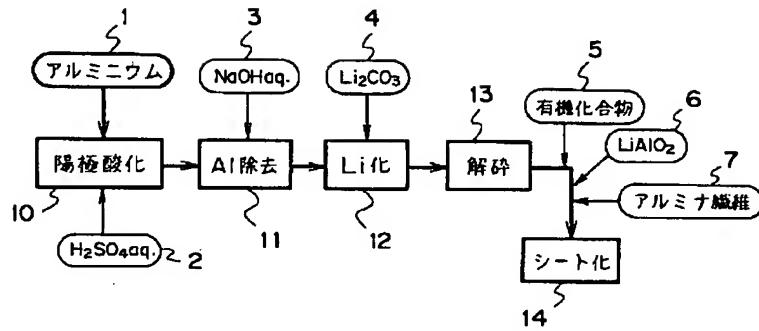
11 アルミニウム除去工程

12 リチウム化工程

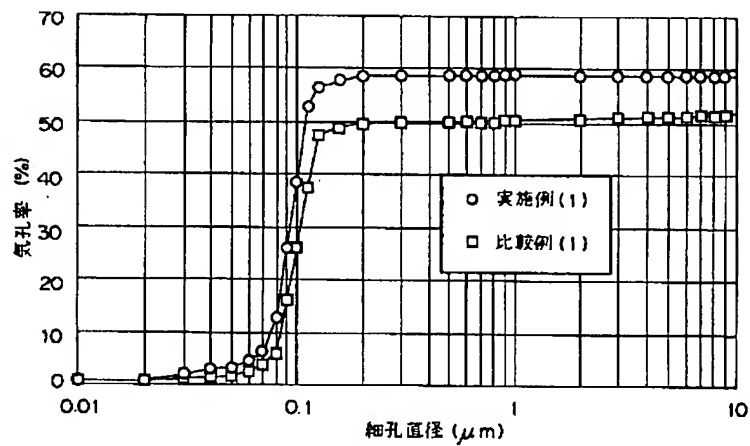
13 解砕工程

14 電解質シート製造工程

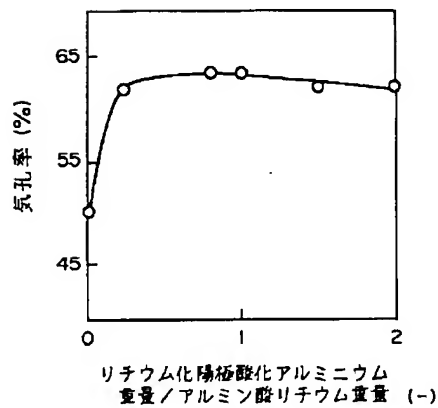
【図1】



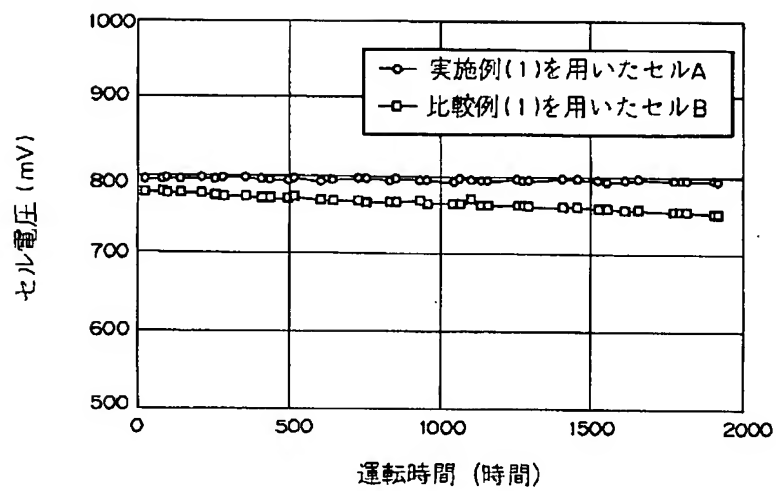
【図2】



【図3】



【図 4】



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